11/10/99 $\langle u \rangle = \int_0^\infty u\,P(u)\,du = \left(\frac{8kT}{\pi m}\right)^{1/2}$

$\sqrt{\langle u^2 \rangle} = \int_0^\infty u^2\,P(u)\,du = \left(\frac{3kT}{m}\right)^{1/2}$

The preceding assumed no molecule-molecule collisions (infinitely small).

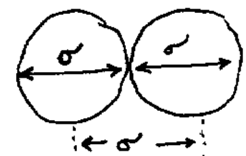
In reality, there are molecular collisions. ⇐ NOW LET'S INCLUDE

⇒ $Z \equiv$ # collisions/sec

Z ought to be $\propto \frac{N}{V}$ ← more molecules, more collisions; ← more volume, less collisions

$\propto \langle u \rangle$ ← faster, more collisions

Assume spherical molecules



$Z \propto \sigma^2$

Therefore:

$$\boxed{Z \propto \frac{N}{V}\sigma^2 \langle u \rangle}$$

In actuality:

$$Z = \sqrt{2}\,\pi\,\frac{N}{V}\,\sigma^2 \langle u \rangle$$

Substituting:

$$Z = 4\sqrt{\pi}\,\frac{N}{V}\,\sigma^2\left(\frac{RT}{M}\right)^{1/2} \quad \frac{\text{\# collisions}}{\text{sec}\cdot\text{molecule}}$$

Then

$$\mathcal{Z} = \frac{\text{\# collisions}}{\text{sec}\cdot\text{vol}} = \underbrace{\left(\frac{N}{V}\right)}_{\text{\# per volume}}\underbrace{\frac{Z}{2}}_{\text{Each collision counted twice}} = 2\sqrt{\pi}\left(\frac{N}{V}\right)^2\sigma^2\left(\frac{RT}{M}\right)^{1/2}$$

Mean free path ≡ average distance traveled between collisions

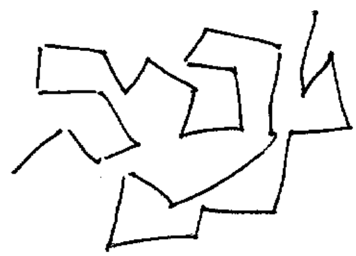
$$\ell = \frac{\overset{\text{dist/sec}}{\langle u \rangle}}{\underset{\text{collisions/sec}}{z}} = \frac{1}{\sqrt{2}\,\pi \left(\frac{N}{V}\right)\sigma^2} = \frac{\text{distance}}{\text{collision}}$$

DIFFUSION — RANDOM WALK

REAL SITUATIONS

Why doesn't O_2 diffuse across a room at $478\ m\,s^{-1}$?

Because it follows a path like:



RANDOM WALK

<u>Mean displacement</u>:

$$\langle d \rangle = \frac{\sum^{\text{all paths}} d_i}{\#\text{ of paths}} = 0$$

<u>Equal</u> probabilities left, right, etc.

$$\langle d^2 \rangle = \frac{\sum^{\text{all paths}} d_i^2}{\#\text{ of paths}} > 0$$

$$= N\ell^2$$

FOR N RANDOM STEPS OF LENGTH ℓ IN ANY DIRECTION

$$\sqrt{\langle d^2 \rangle} = \sqrt{N}\,\ell$$

<u>FOR A GAS</u>

$$\langle d^2 \rangle = \underset{\#\text{ collisions/sec}}{z}\,\ell^2$$

ℓ: mean free path (see above)

$$\langle d^2\rangle^{1/2} = \sqrt{z}\, \ell = \frac{\langle u\rangle}{\sqrt{z}}$$ (because $\langle u\rangle = z\ell$)

EXAMPLE MOLECULE OF N_2

$$\langle d^2\rangle^{1/2} = \sqrt{z}\,\ell$$

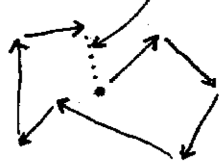
$$z = 4\sqrt{\pi}\, \underbrace{\frac{N}{V}}_{\frac{N_0 P}{RT}}\, \underbrace{\sigma^2}_{3.74\text{Å}} \left(\frac{RT}{M}\right)^{1/2} = 7.27 \times 10^{9}\ s^{-1}$$

298K

MW of N_2

$$\ell = \frac{1}{\sqrt{2}\,\pi \frac{N}{V}\sigma^2} = 6.53 \times 10^{-8}\ m$$

$$\therefore \quad \langle d^2\rangle^{1/2} = \left(7.27\times10^{9}\ s^{-1}\right)\left(6.53\times10^{-8}\ m\right) = 0.557\ cm$$



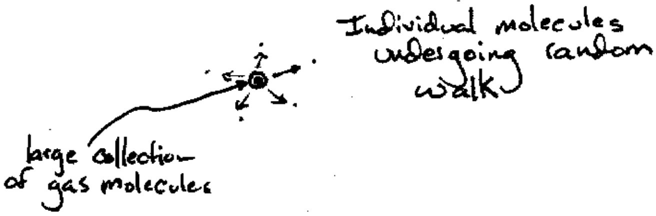
While $z\ell$ = (collisions/sec)(distance/collision)

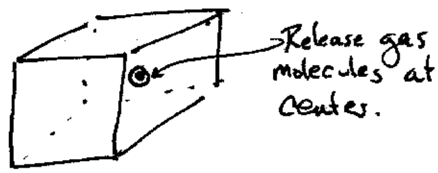
= 475 m (sum of lengths of solid arrows)

Big difference: 0.557 cm vs. 475 m

$\frac{\text{Net displacement}}{\text{sec}}$ $\qquad$ $\frac{\text{total distance}}{\text{sec}}$

Diffusion - Collective random walks

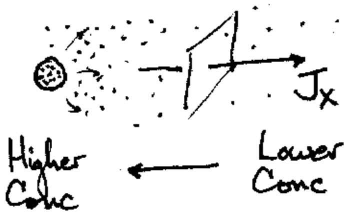




Q:

A) What happens?
→ gas distributes uniformly

B) Why?
→ Second Law - increased entropy
— spontaneous



J_x = Flux in x-direction

$$\text{Flux} \equiv \frac{\text{net transport (moles)}}{(\text{Area})\,(\text{Time})} = \text{mol cm}^{-2}\,\text{s}^{-2}$$

(typo Fig 6.4 legend)

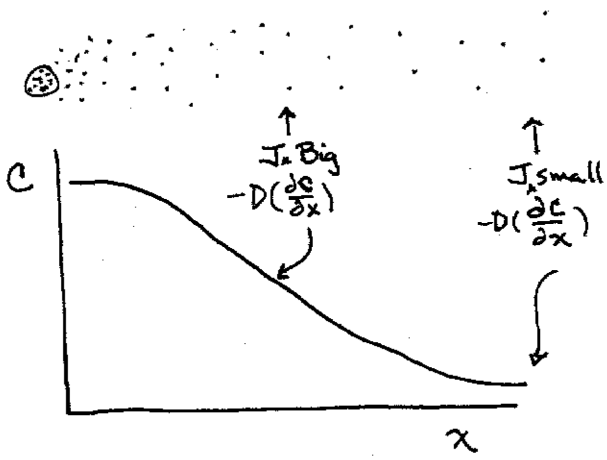
Q: What is the flux at equilibrium?
A: $\emptyset$

Diffusion Coefficient

Fick's 1ST Law $\quad J_x = -D\dfrac{\partial c}{\partial x}$

Flux is proportional to conc. gradient

Larger gradient ⟶ Larger flux

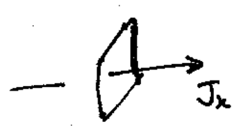


How does J_x vary with distance (and time)?

Fick's 2^{ND} Law

$$\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)$$

Measuring Flux and D (diffusion coefficient)

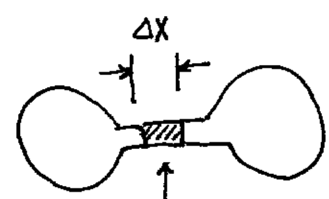


Monitor passage of molecules through a hole of fixed/known dimension

Measure conc. gradient

$$D = -J_x\left(\frac{1}{\frac{\partial c}{\partial x}}\right)$$

$$= -J_x\left(\frac{\Delta x}{c_2 - c_1}\right)$$

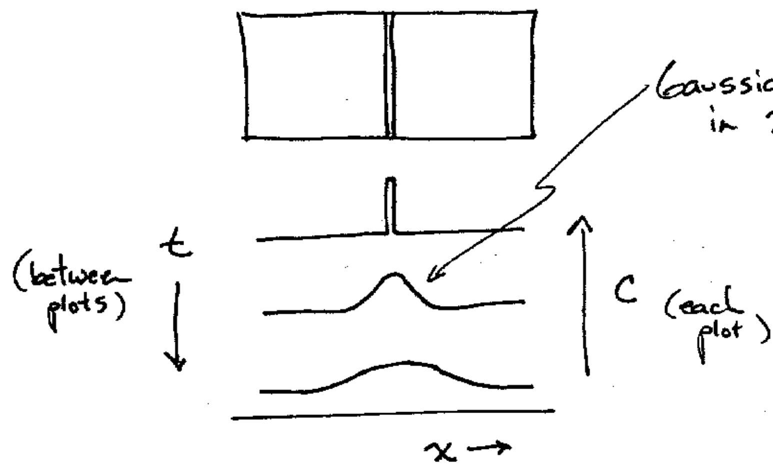


porous glass disk or other material through which we wish to measure diffusion.

Einstein 1905

$$\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t \quad \text{Integrate} \Rightarrow \quad C = \frac{\omega}{(4\pi D t)^{1/2}}\, e^{-x^2/4Dt}$$

Gaussian in x → Ae^{-bx^2}

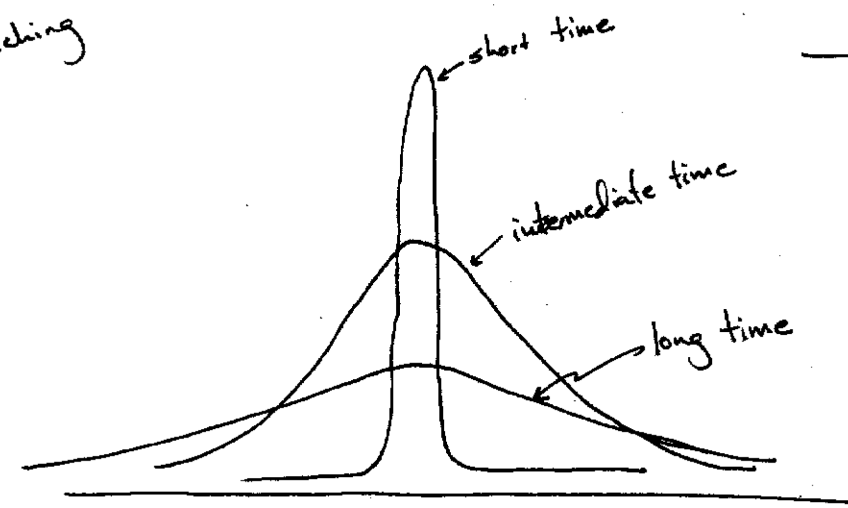


From the above, derive

$$\langle x^2 \rangle = 2Dt$$

$$\therefore \quad D = \frac{\langle x^2 \rangle}{2t}$$

Fluorescence Photo Bleaching



The "spread" vs time measures D

Full width at half max $= 4\sqrt{\ln 2\, D t}$

$$\tfrac{1}{2}(\cancel{-}) = (\cancel{-})\, e^{-w^2/4Dt}$$

$$-\ln 2 = -w^2/4Dt$$

$$w^2 = (\ln 2)\, 4Dt$$